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Polysaccharide separation mechanism in polysulfone-Fe_3O_4 magnetic composite membranes

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Polysulfone (PSF)-Fe_3O_4 composite membranes were prepared by the phase-inversion process and their polysaccharide separation mechanism was explored using chondroitin sulfate (CS) and dextran. The mechanism was analyzed from constraints on the magnetic field and geometric deformation. It was found that variations in dextran rejection from 58% to 46% were mainly influenced by the geometric deformation of the composite membrane, while the magnetic field had a significant influence on variations in CS rejection from 82% to 35%. The results indicate that it is possible to continuously separate different types of polysaccharide with a composite membrane by adjusting the external magnetic field.

magnetic composite membrane, polysulfone-Fe_3O_4, dextran, chondroitin sulfate

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Ultrafiltration (UF) is a pressure driven membrane separation process that separates particulate matter from soluble components in the carrier fluid (such as water) [1]. Membrane separation technologies have been widely used in pharmaceutical, chemical, food, biological engineering, environmental protection, metallurgy, electronics and other fields [2–5]. Magnetic nanoparticles are useful for a wide range of applications from data storage to magnetic composite membranes. The large-scale preparation of Fe_3O_4 nanoparticles enhances this potential [6,7]. With the development of nanomaterials and nanotechnology, the use of inorganic nanomaterials for the preparation of inorganic-organic composite ultrafiltration membranes was proposed. To date, extensive research has been carried out on the selection of optimal preparation conditions. For a given membrane polymer, it has been found that the type of additive is a crucial factor in determining membrane structure and properties [8,9].

Recently, with the rapid increase in research into polysaccharide biological activity, separation technology of polysaccharides has emerged as a hot topic. Membrane separation is a mature technology that can be used to separate various mixtures of liquid materials in a growing range of applications [10]. Because the system has significant separation efficiency, does not undergo phase-change and does not compromise biological activity, it is particularly suitable for the separation and purification of polysaccharides [11].

The nonmagnetic polysaccharide dextran is a complex, branched glucan composed of chains of varying lengths [12–14] that was initially selected to explore geometric deformation. On the other hand, for the acidic polysaccharide chondroitin sulfate [15], which possesses a large number of negative charges and is highly hydrophilic and viscoelastic, there is generally serious ultrafiltration membrane fouling and concentration polarization. Research shows ultrafiltration successfully separates and purifies components from mixtures by changing the external magnetic field and ionic strength to obtain nearly 100% target product purity [16]. Based on the Lorentz force ($F=qvB$), CS rejection was altered through variation in an external magnetic field.

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Nanosized Fe_3O_4 particles encased by oleic acid were expected to distribute homogeneously within the membrane [17]. On one hand, when the composite membrane was in a magnetic field, the Fe_3O_4 nanoparticles would bring deformation to the skin layer and pore structure. On the other hand, specific CSs passed through a PSF-Fe_3O_4 composite membrane either more easily or with more difficulty in a magnetic field. By adjusting the magnetic field therefore, different substances are expected to pass differently through a composite membrane [18].

In our previous studies, the preparation of a polysulfone-Fe_3O_4 composite membrane and its behavior in a magnetic field was investigated [12]. However, the ultrafiltration mechanism of PSF-Fe_3O_4 for polysaccharides is unknown. Polysaccharides dextran and CS were therefore used in the membrane separation reported in this article and the effect of separation and mechanisms analysis are described through this novel, practical experiment.

1 Experimental

1.1 Materials

Polysulfone ($[\eta] = 0.62$) was purchased from the ShuGuang Chemical Plant in Shanghai, China. Fe_3O_4 nanoparticles encased in oleic acid (8–12 nm in size) were purchased from the Anhui Jinke Magnetic Liquid Co. Ltd. Polyethylene glycol (PEG) with average molecular weight of 400 and dimethylformamide (DMF) were supplied by the Shanghai Chemical Regents Company. Dextran T-10, T-40, T-70, T-100 and T-200 were from Pharmacia, Sweden. Chondroitin sulfate was supplied by Anhui Chem-Bright Bioeng Co., Ltd. All chemicals were of commercial analytical grade.

1.2 Preparation of membranes

PSF-Fe_3O_4 composite membrane was prepared by the phase-inversion method [12]. Polymer dope consisting of PSF (15% by weight of solution), PEG (2% by weight of solution) and DMF (83% by weight of solution) were dissolved at about 60°C for 3 h with vigorous stirring. After a uniform polymer dope was formed, nanosized Fe_3O_4 particles were added to the dope with vigorous stirring for 3 h.

1.3 Experiments with membranes using dextran

(i) Interchange magnetic field. Dextran T-40 solution was prepared and the membrane was pre-pressured through magnetic ultrafiltration devices, as shown in Figure 1, at 0.5 MPa for 30 min. At 20±1°C and 0.1 MPa, the changes in dextran T-40 rejection of a conventional PSF membrane and PSF-Fe_3O_4 composite membrane were investigated with and without a magnetic field. For PSF ultrafiltration, a magnetic field of 0.4 T was used, while magnetic fields of 0.2 and 0.4 T were used in the case of the PSF-Fe_3O_4 ultrafiltration. The fluid was collected after flux reached steady state and tested every 5 min, the two cases that in the presence and absence of electromagnetic fields were alternated every 15 min, respectively. The total sugar content and the rejection were calculated based on the phenol-sulfuric acid method [19] with absorbance measured at 490 nm. Once the magnetic field was changed, the operation was interrupted for 30 s to allow the Fe_3O_4 particles to magnetize or demagnetize fully and the deformation of membrane caused by the Fe_3O_4 particles to be completed.

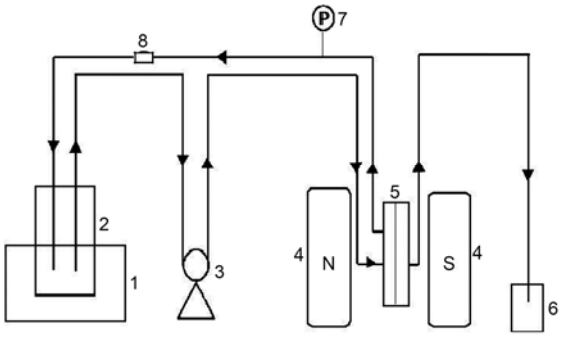

Figure 1 Schematic of the magnetic ultrafiltration equipment. 1, Constant temperature bath; 2, feed tank; 3, pump; 4, galvanized magnet; 5, membrane cell; 6, collection tank; 7, pressure gauge; 8, throttle.

(ii) Varied magnetic field. Experimental conditions and processes were the same as those described in Section 1.3(i), with magnetic field changes of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 T, respectively in the ultrafiltration tests. The subsequent operations were carried out as described in Section 1.3(i) and the rejections were calculated.

(iii) Water flux experiments. The membrane sample was pretreated with deionized water for 30 min under a pressure of 0.2 MPa until the water flux was stable. The intensity of the external magnetic field was increased gradually at a rate of 0.2 T/time until the magnetic field strength reached 1.2 T. Water flux was recorded every 5 min and the electromagnetic fields tuned every 10 min.

1.4 Experiments on composite membranes using CS

To accurately determine the effect of the PSF-Fe_3O_4 composite membrane on the rejection of CS, an approximately similar molecular weight of dextran was selected for comparison. Thus, the relative molecular weight of CS had to be determined first. Then, 1 mg/mL standard solutions of dextran T-10, T-40, T-70, T-100, T-200, T-500 were prepared and their retention times, t, determined by ELSD-HPLC. With t as the abscissa and the natural logarithm of dextran molecular weight, logMw, on the vertical axes, a standard curve for molecular weight estimation and the corresponding regression equation was obtained.

CS solution was prepared and its rejection determined under varied magnetic field circumstances, as described in

Section 1.3(ii). Experimental results under varied magnetic field were compared with the dextran molecular weight standards.

CS solution was prepared, and the membrane was pre-pressured at 0.5 MPa for 30 min. The rejection of CS by the PSF-Fe_3O_4 composite membrane was detected at pressures of 0.1, 0.2 and 0.3 MPa.

2 Results and discussion

2.1 Analysis of dextran rejection at different conditions

(i) The effect of the magnetic field on dextran rejection of the membranes at changing magnetic field. The rejection of dextran T-40 by the general PSF membrane in the presence (30–45, 60–75, 90–115 min) and absence (45–60, 75–90 min) of the magnetic field is shown in Figure 2. The rejection was independent of the external magnetic field, although a slight increase in retention time observed may be related to membrane contamination in the final stages. As seen in Figure 3, the rejection of PSF-Fe_3O_4 composite membrane for dextran T-40 was reduced when the external magnetic field was applied. At a magnetic field strength of 0.2 T, rejection dropped very slightly from 58% to 53%, while in a magnetic field of 0.4 T, it dropped to around 46%. The rejection was immediately restored when the field was removed.

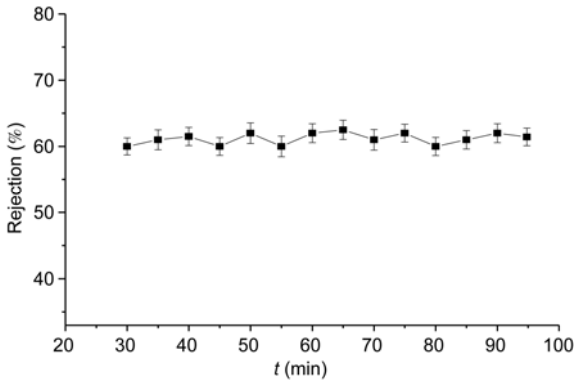

Figure 2 Rejection of dextran T-40 by the PSF membrane with and without the magnetic field.

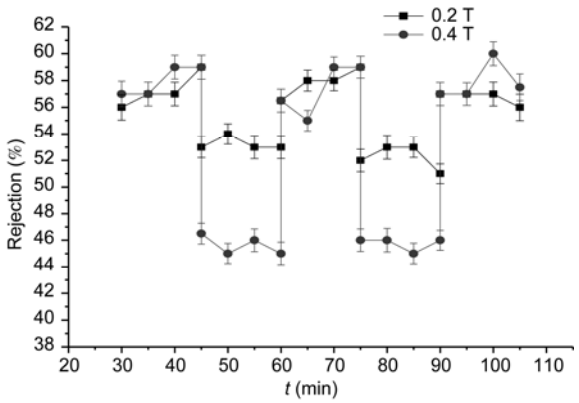

Figure 3 The rejection of the PSF-Fe_3O_4 composite membrane with and without the magnetic field.

From Figures 2 and 3, it can be seen that the rejection of dextran by the PSF-Fe_3O_4 composite membrane was reduced in the magnetic field while that of the PSF membrane was unchanged. This behavior may be due to the following tentative mechanisms.

First, the nano-Fe_3O_4 particles had a magnetostriction effect, with a magnetostriction coefficient λ of 39×10^{-6}, $\lambda>0$. Under the action of an external magnetic field, the size of the largest pores would significantly impact the membrane's rejection characteristics [20].

Second, nano-Fe_3O_4 distributed in the membrane displayed superparamagnetism, which would reverse under an externally applied magnetic field, arranged along the field direction, which would cause membrane skin layer and membrane pore deformation. As a result, permeation of dextran T-40 under external magnetic field would be increased and its rejection reduced [21].

Third, as dextran is an anti-magnetic material, it suffers a weak force in a magnetic field when it permeates through a magnetic membrane. Adsorption of the membrane decreased, which can help passage through the membrane and lower rejection when passing through the membrane skin layer and porous layer.

(ii) The effect of magnetic field on dextran rejection by the membrane at varied magnetic field. As can be seen in Figure 4, the variation of rejection of dextran T-40 did not show a straight linear relationship with increasing magnetic field strength. In the range of 0–0.6 T, the rejection of dextran T-40 decreased as the magnetic field strength increased. The membrane pore size increased over the range of this magnetic field, which is consistent with the results described in Section 2.1(i). Over the range of 0.6–1.2 T, the rejection of dextran increased as the external magnetic field strength increased, whereas the pore size decreased in this magnetic field range.

With increasing magnetic field strength, two different states of the particles impacted on the membrane pore sizes,

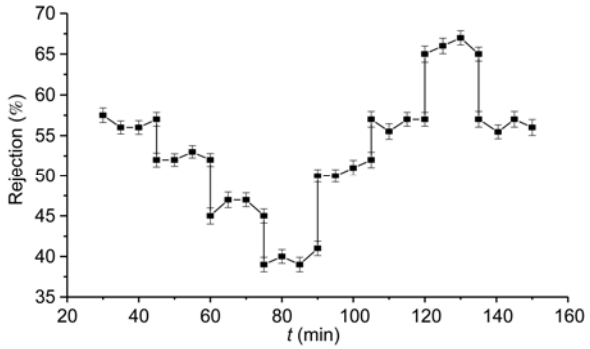

Figure 4 The rejection of the PSF-Fe_3O_4 composite membrane under various magnetic fields.

for which an interaction mechanism was proposed. When the magnetic field strength was in the range of 0–0.6 T, one type of state played a major role, with variation of membrane pore size in one direction. As the magnetic field strength moved outside the range of 0.6–1.2 T, another state played a major role and membrane pore size changed in the opposite direction.

(iii) The effect of magnetic field on pure water flux of the two types of membrane. Figure 5 shows that in the range of 0–0.6 T (30–60 min), water flux for the PSF-Fe_3O_4 magnetic membrane increased slightly with increasing magnetic field. In contrast, over the range of 0.6–1.2 T (60–90 min), water flux showed a reverse trend with increasing magnetic field strength, similar to the variation of dextran T-40 rejection with the PSF-Fe_3O_4 magnetic membrane. However, because the porosity of the PSF membrane with a changing magnetic field had not been adjusted, there was no significant change in pure water flux.

2.2 Analysis of CS rejection at different conditions

(i) The effect of magnetic field on CS rejection by the membranes with variation of the magnetic field. According to the standard curve in Figure 6, the relationship between retention time and natural logarithm of molecular weight for standard dextran with molecular weights of 10–100 kD was linear. The regression equation was logMw = 8.41486–0.46346t, R^2 = 0.9928.

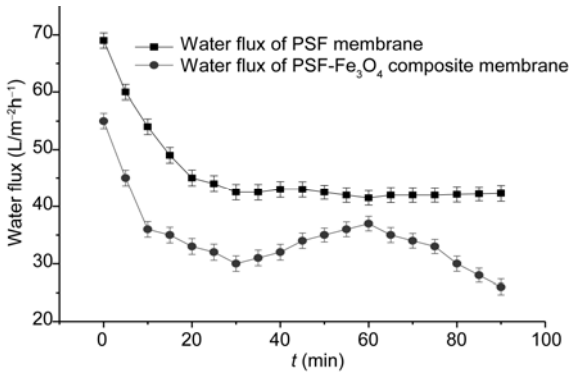

Figure 5 Water flux with and without the magnetic field.

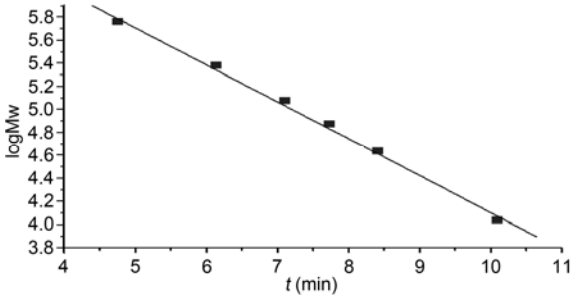

Figure 6 Standard curve for molecular weight determination of polysaccharides.

The retention time for CS was 7.604 min (Figure 7) which, according to the standard curve in Figure 6 gives a molecular weight of about 98 kD, which is approximately similar to dextran T-100 (Mw = 110 kD). Therefore, dextran T-100 was chosen as the control.

It can be seen in Figure 8, that at varied magnetic field, rejection of dextran T-100 first decreased and then increased, consistent with rejection of dextran T-40 in a varied magnetic field. By increasing the magnetic intensity, the rejection of CS of approximately similar molecular size decreased continuously. However, the extent of the reduction decreased gradually. Because CS contains a large number of negative charges, not only would CS bear the Lorentz force ($F = qvB$) but the rejection would be influenced by the geometric deformation of the membrane pore itself under the external magnetic field. The variation of rejection was caused by magnetic intensity. That may, tentatively, be due to the following types of mechanism.

First, the superparamagnetic Fe_3O_4 nanoparticles could produce an induced magnetic field under the influence of an externally applied magnetic field. The induced magnetic field and magnetic field together would form a composite magnetic field, with a direction that can be decomposed into vertical and horizontal components. When the negatively charged CS molecular passed through the skin layer of the magnetic membrane, not only suffered a vertical downward

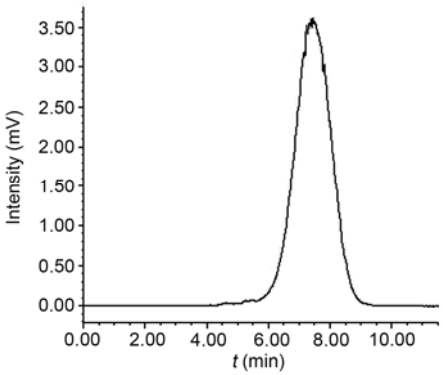

Figure 7 ELSD-HPLC chromatogram of CS.

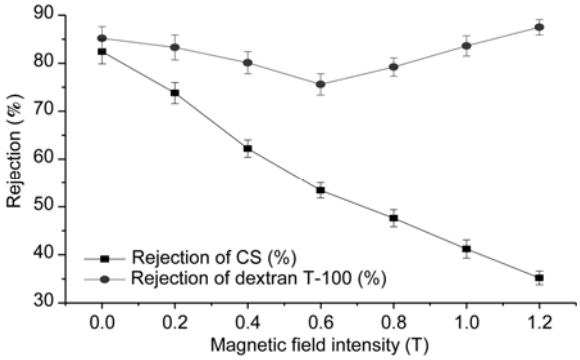

Figure 8 Comparison of rejection of dextran T-100 and CS in a varied magnetic field.

force but was also subjected to the magnetic field strength along the horizontal direction of the membrane surface in the composite magnetic field. The composite magnetic field caused CS molecules to undergo circular motion to adopt a movement downward through the spiral membrane of the skin layer. Concentration polarization was consequently weakened so that CS molecules passed through the epidermis of the membrane more easily.

Second, the CS molecules with a large number of negative charges underwent spiral movements, so there would be an induced magnetic field under the external magnetic field. Thus, CS molecules could be seen as small magnets attracted by the magnetic field and permeated through the PSF-Fe_3O_4 membrane more easily.

Third, the charged molecules of CS have an electric dipole, one end of which can be considered to accumulate positive charge, while the negative charge can fairly be considered to be gather together at the other end. Charged molecules in a magnetic field will bear a torque, by which it is rotated in a magnetic field (Figure 9). Furthermore, all molecules have unique magnetic properties, which causes the arrangement of molecules in a magnetic field to align parallel to the direction of the magnetic field. Rotation of the CS molecule would make it easier to permeate through the membrane.

Finally, superparamagnetic Fe_3O_4 nanoparticles distributed in the membrane would twist as they attempt to arrange along the magnetic line of force and bring deformation of the skin layer and pore structure. Results show that the deformation was influenced the permeation through the membrane.

(ii) The effect of magnetic field on CS rejection of the composite membranes at different pressures. Figure 10 shows the rejection by the PSF-Fe_3O_4 composite membrane with and without different magnetic intensities at pressures of 0.1, 0.2 and 0.3 MPa, respectively. The decline in rejection in the magnetic field was more obvious at lower pressure. It should have little relationship with the fourth mechanism, because the operation was interrupted for 30 s with each cycle, the condition of the magnetic field was altered

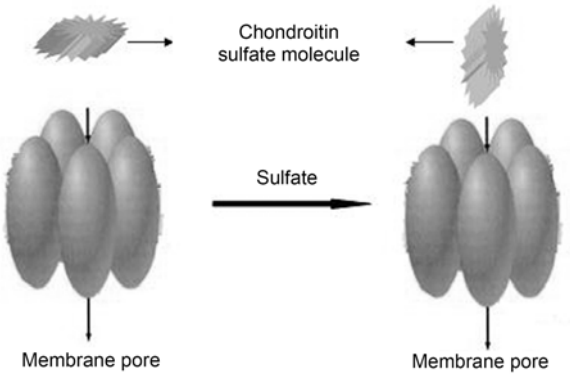

Figure 9 Schematic of the turn of the CS molecule when passing through the membrane.

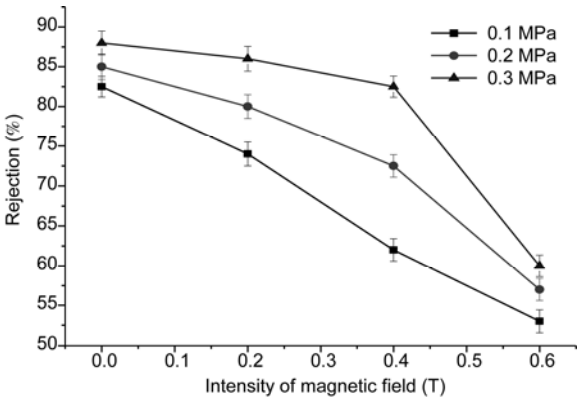

Figure 10 The rejection of CS with and without different magnetic intensities at different pressures.

so as to make the Fe_3O_4 particles fully magnetized or demagnetized, so the deformation of membrane caused by Fe_3O_4 particles had been accomplished before the pressure was applied. The phenomena shown in Figure 10 may be explained as follows. With an increase in upstream pressure, the horizontal velocity decreased, so that the magnetic field force decreased and CS molecules passed through the membrane more rapidly. There was a shortened time for the effect of magnetic field on CS molecules.

3 Conclusion

This paper focused on the performance of a PSF-Fe_3O_4 composite membrane in a magnetic field. The separation mechanisms for geometric deformation and magnetic field constraint were analyzed. For a nonmagnetic material (dextran), the rejection was mainly affected by variation of geometric deformation of membrane pores; for the charged material (CS), the variation of rejection was mainly caused by the magnetic field.

We developed a method based on changes in rejection of polysaccharides. This method may continuously separate different types of polysaccharides by adjusting the external magnetic field and provide a better understanding of magnetic composite membranes. Further investigations into the composite magnetic membrane will be carried out in the future to develop this novel idea.

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